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Coordination diversity of *N*-phosphoryl-*N*′-phenylthiourea (LH) towards Co^{II}, Ni^{II} and Pd^{II} cations: Crystal structure of ML_2-*N*,*S* and ML_2-*O*,*S* chelates

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Abstract

Thiourea, $PhNHC(S)NHP(O)(OPr^i)_2$ (LH) chelates of Co^{II}, Ni^{II}, and Pd^{II} ions have been obtained and investigated by single-crystal X-ray diffraction, UV, IR, NMR spectroscopy, and EI mass-spectrometry. The unusual 1,3-*N*,*S*-coordination via sulfur and NP(O) nitrogen atoms has been found in the *trans*-square-planar NiL_2 and PdL_2 complexes, whereas the 1,5-*O*,*S*-coordination is realized in the tetrahedral CoL_2 complex. DFT calculations have revealed significant stabilization of the 1,3-*N*,*S*-structures due to stronger crystal field and the NH–O=P hydrogen bonds.

Keywords: Thiourea coordination; Substituent effects; Co^{II} complexes; Ni^{II} complexes; Pd^{II} complexes; *N*,*S*-coordination; *O*,*S*-coordination

1. Introduction

β-Dicarbonyl compounds (*N*-acylureas **1**, acetylacetonates, etc.) and their phosphorus containing analogs (*N*-acylamidophosphinates **2**, imidodiphosphinates **3**) (Fig. 1) were found to be very attractive ligands for variety of metal ions [1–4].

β-Bifunctional ligands **1**–**3** contain three potential donor centers: X, Y and internal nitrogen atoms. Nucleophilic ability of the latter donor is significantly reduced by the two neighboring electron-withdrawing groups. That is why the alkylation of *N*-thioacylamido(thio)phosphates-$RC(S)NHP(Y)(OR')_2$ (Y = O,S) always proceeds on the thiocarbonyl sulfur atom [1a,5].

There is a fair amount of the data concerning the structures of complexes of divalent transition metal ions of Ib, IIb, VIIIb groups with *N*-thioacylamidothiophosphinates (**2**) (X, Y = S) [1–5,7–10]. The 1,5-bidentate coordination of deprotonated ligands through sulfur atoms takes place in all these cases.

The substituents (or other factors) are hardly capable of changing a coordination mode in the complexes of *dithio*-derivatives of **2** with divalent cations of VIIIb group. Due to the strong π-interactions, the formation of metal–sulfur bonds is most energetically favorable in all these cases.

Replacement of one sulfur atom in conjugated $[RC(X)NP(Y)R'_2]^{(-)}$ moiety to oxygen (X = S, Y = O or X = O, Y = S) leads to appearance of the ambivalent coordination modes and possible competition between the three donor centers in the binding anion species. As a result, the

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